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               SPECTRA OF DIFFUSE REFLECTION AS AN INFORMATION SOURCE ABOUT TH--ETC(U)
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SPECTRA OF DIFFUSE REFLECTION AS AN INFORMATION SOURCE ABOUT THE ABSORPTION SPECTRA OF ADSORBED MOLECULES

(Kotov, Ye. I.; Spektry diffuznogo otrazheniya kak istochnik informatsii o spektrax pogoloshcheniya adsorbirovannykh molekul, Teoreticheskiye i prikladnyye problemy rasseyaniya sveta, 1971, pp. 387-395; Russian)

Optical spectral methods are being ever increasingly used in inves-   /387
tigations of adsorption and catalysis where objects characterized by
strong light scattering are encountered /1,2/. Among these objects are
disperse powders of solid substances having a particle size of 10-250 μm   MICRO M
on whose surface molecules are adsorbed.

The adsorption of molecules, the formation of transition compounds
and end products as the result of a heterogeneous catalytic reaction are
manifested in optical electron spectra which reflect the state of the
outer electrons of the molecules and atoms and contain valuable informa-
tion on the mechanism of processes acting on the surface.

Some valuable information on the character of the local interaction
of molecules with active centers of the surface of adsorbents or catalysts
can be garnered from the absorption spectra of adsorbed molecules in the
200-1000 nm region.

To clarify the meaning of the information, we shall examine some char-
acteristics of the interaction of molecules with the surface of a solid
body and of the light absorption by adsorbed molecules.

Molecules on the Surface of a Solid Body. In actuality the case often
occurs where molecules from the gaseous phase strike the surface of a solid
body, remain on the surface in the state of physical adsorption throughout
the life span of the adsorbed state, and then, as the result of desorption,
again escape into the surrounding volume. The state of physical adsorption
corresponds to this state of the molecule when its electron shell retains
its individuality, experiencing only negligible disturbance in the surface   /388
force field, and the distance between the surface and the atom of the mole-
cule closest to it is comparable to the distance between the closest atoms
of adjacent molecules in liquids. In such cases the interaction of mole-
cules with the surface is described by a potential energy curve similar to
curve 1 in fig. 1, where the adsorption energy Ea is several kilocalories
per mole.

The action of the force field of the surface on the electron shell of
the adsorbed molecule results in a change of the relative distance between
the energy levels of the molecule as compared with the gaseous state. If
in the gaseous state a molecule absorbs a light quantum $h\nu_{gas}$, then in the
adsorption state it, as a rule, absorbs a light quantum $h\nu_{ads} \neq h\nu_{gas}$, since

the imaginary curve of the potential energy for a molecule in the excited state (curve 1* in fig. 1) differs from the curve of the potential energy for a molecule in the base state and $Ea \neq Ea^*$, $r_0 \neq r^*$. The interaction of the molecule with the surface facilitates the washing away of the vibrational structure of the electron bands in the adsorption spectra of adsorbed molecules. As a result, it becomes more similar to the absorption spectra of solutions than to the absorption spectra of the vapors of the molecules under study /3,4/.
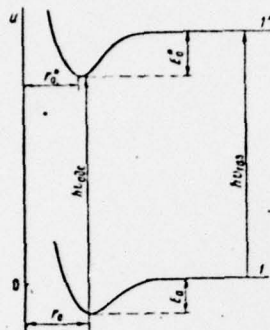

Fig. 1. Potential energy curves (U): 1-adsorption of molecule in base state; 1*-same in excited state; Ea, Ea^*-adsorption energy; r_0, r_0^*-equidistance of molecule from surface.
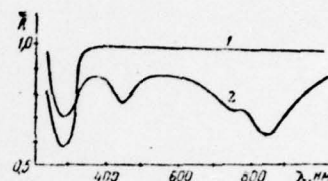
Fig. 2. Differential spectra of diffuse reflection measured after benzidine adsorption. 1-inactive silica gel; 2-active alumosilica gel.

In the physical adsorption state the molecules can displace along the surface (two-dimensional gas), thereby overcoming the relatively low potential barrier between adsorption centers due to the heat energy of motion. Thanks to this, the molecules can encounter "active" adsorption centers which can be foreign extrinsic atoms in a lattice, defects, and so on. And as a result of contact with them go into the chemical adsorption state (chemosorption), when the adsorption energy is several tens of kilocalories per mole, and the distance between the surface and the atom of the molecule closest to it is comparable to the distance between atoms in the same molecule.

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As the result of the interaction with the active centers the bonds between atoms in a molecule can change substantially, break down, or form new ones, including ones with the surface atoms. In such cases compounds of the molecular type are formed that can differ considerably from the initial molecules and have its own individual absorption spectrum (fig. 2).

On the basis of what has been presented the following independent problems may be identified: investigation of molecules in the physical

adsorption state (determination of the absorption band shift and change in value of molecular absorption coefficient, caused by action on the molecules of surface force field); study of the products having a profound molecular transformation (measurement of their absorption spectra, determination of character of those profound changes and transformations on basis of spectrum that have occurred with the molecule as the result of contact with active centers of surface; ascertaining the nature of the active centers causing specific transformations of the molecules).

It follows from this that together with determining the numerical values of the molecular coefficient of absorption of the adsorbed molecules k_{ads} the qualitative form of the spectra $k_{ads}(\lambda)$ assumes great importance, making it possible on the basis of the form of the spectral curves to establish the nature of the products of profound molecular change. Most authors using spectral methods in investigations of adsorption and catalysis are currently restricting themselves to the last named problem.

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The molecular coefficient of absorption of adsorbed molecules k_{ads} has the same physical sense as k for molecules in a solution. If for solutions the spectral relationship $k(\lambda)$ is found comparatively easily by measuring transmission $T\lambda = I/I_o$ and calculating $k\lambda$ by means of the Bouguer-Lambert-Behr law: $T = I/I_o = e^{-knl}$ (k is the molecular coefficient of absorption, n is the number of absorbing molecules in 1 cm^2 of solution, l is the thickness of the absorbing layer), then in the case of adsorbed molecules the problem of obtaining the spectral relationship $k_{ads}(\lambda)$ is greatly complicated by light scattering in the specimen. Therefore instead of measuring the transmission spectrum $T(\lambda)$ the diffuse reflection spectrum $R(\lambda)$ is measured; it contains information on light absorption by adsorbed molecules.

It is most desirable to use the so-called "semiinfinite" light-scattering layer, i. e., limited on the illuminated side by a plane and of sufficient thickness and extent as to disregard the light passing through and sideways. We shall distinguish the spectra of diffuse reflection from the "semiinfinite" layer: absolute $R(\lambda)$, relative $R(\lambda)$, and differential $R(\lambda)$ representing the spectral dependence of the value of the corresponding coefficients of diffuse reflection on wavelength.

The absolute coefficient of diffuse reflection R is the ratio of the diffusely scattered light flux to the incident. In the case of monochromatic light illumination we shall examine $R\lambda$ as the ratio of the photon number N_o departing from the outside surface of the layer within the limits of the external hemisphere to the photon number N_o impacting from outside on the outside surface of the layer per unit of time: $R\lambda = No/N_\phi$.

In the case where the diffusely reflected light flux is not compared to the incident light flux, but rather to the diffusely reflected by another specimen, for example, by a comparison standard, we then refer to a'

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relative coefficient of diffuse reflection $\bar{R}$, since the magnitude and spectral characteristic of the latter depends on the selection of the comparison standard. In the case of monochromatic illumination we shall assume that $\bar{R} = No/No_{stand}$.

The differential spectrum of diffuse reflection $\bar{\bar{R}}(\lambda)$ is a particular case of the relative spectrum of diffuse reflection, often used in the study of the absorption spectra of adsorbed molecules. In this case the adsorbent itself without the adsorbed molecules is used as the comparison standard.

Adsorbent-Multipath Tray Light-Reflecting Layer. To show even more graphically how light absorption by adsorbed molecules manifests itself in the differential spectra of diffuse reflection, we shall use the concept of "semiinfinite" light-scattering layers of adsorbent without adsorbed molecules in the form of a "multipath tray."

Let us imagine that a monochromatic light beam strikes the outside surface of a layer. Light of a given wavelength is not absorbed by the substance of the adsorbent ($n = 0$) and No is equal to the number of photons that are diffusely reflected by the layer per unit of time within the limits of the external hemisphere. No includes photons that are subject to a definite statistical function of distribution along the path passed by a photon in the light-scattering layer before exiting outside. If this function is known, No can be presented in the form of the sum $\sum \Delta N_{oi}$, where the first term ΔN_1 equals the number of photons that pass in the layer a path having a length from 0 to d apiece, the second term N_{02} is the number of photons whose path length is from d to 2d, the third term ΔN_{03} -- from 2d to 3d, and so forth, where d is some selected length segment.

Now it is possible to build an optical model of the light-scattering layer in the form of a set of elementary optically transparent trays of different length having the dimensions: $dxdx\frac{1}{2}d$, $dxdx$, $dxdx\frac{3}{2}d$, $dxdx\frac{5}{2}d$, ..., through which ΔN_{01}, ΔN_{02}, ΔN_{03}, ΔN_{04}, ... the number of photons per time unit pass (the number of elementary trays depends on the selection of d).

Let us now assume that the adsorption of the substance under study has occurred. When there are small concentrations of adsorbed substances, the molecules can deploy in the surface at great distances from each other, thereby making it possible to disregard light scattering by the adsorbed substance, and to consider only absorption, and to use the model of the "multipath tray" for calculations using the formula

$$R_\lambda = \frac{\sum_{i=1}^{\infty} \Delta N_{oi} e^{-k_{nc} n l_i}}{\sum_{i=1}^{\infty} \Delta N_{oi}}, \qquad (1)$$

where n is the number of adsorbed molecules in 1 cm^3 of the light-scattering medium, given a uniform distribution inside the layer, l_i is the length of

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the elementary tray: $l_i = (i - \frac{1}{2})d$.

Position of Maxima of Absorption Bands of Adsorbed Molecules in
Spectra of Diffuse Reflection. The absorption of light by adsorbed
molecules manifests itself in the spectra of diffuse reflection dif-
ferently depending on the concentration of adsorbed substance /5/.
When there are small concentrations, when it is possible to disregard
the supplemental light scattering in the sample caused by the presence
of the adsorbed phase, it is natural to expect that the minima in the
spectral curves $\bar{R}(\lambda)$ will be found at the same values of λ as are the
maxima in the spectra of $k_{ads}(\lambda)$. In reality, this is not always so.

In practice, the differential method is often used employing two
similar trays filled with adsorbent. In one of them the adsorption
takes place, while the other serves for comparison in spectrophotometry.
Before the adsorption of the molecules, for checking purposes the com-
parison spectrum is measured. On the graph it appears as a straight
line parallel to the wave length axis, since similar light-scattering
layers of the adsorbent studied can be examined as two identical "multi-
path trays."

It must be noted however that the comparison spectrum does not
reflect those changes that the "multipath tray" undergoes itself with
change in the wavelength of the incident light, thanks to the change
of the scattering and absorption capability of the adsorbent sample.

The "multipath tray" will inevitably spontaneously become deformed
due to change both in the No number as well as the distribution function
No along the path length passed by the photon in the light-scattering
layer, for example, in moving to a region of the spectrum where the ab-
sorbent itself begins to absorb light notably. To these effects may be
added the circumstance when measuring spectra of adsorbed molecules, it
is easy to understand in the example of the differential spectra of trans-
mission of solutions, having assumed that the optical length of both trays,
with the solution and solvent, is synchronously changed by an uncontrolled
specimen when scanning the spectrum.

We shall examine two cases: 1) a "multipath tray" retains its dimen-
sions and form during spectrum scanning, 2) a "multipath tray" deforms
during spectrum scanning. In measurements of $\bar{R}(\lambda)$ in the visible range,
the first case can be practically realized if optical glass powder is used
as adsorbent, and the second case can be if colored glass is used as ad-
sorbent.

Fig. 3 presents differential spectra of diffuse reflection measured
after the adsorption of Nd_2O_3 in optical glass and colored glass powders
in the 710-740 nm range where Nd_2O_3 has three absorption maxima. In the
first case (curve 1, Fig. 3) the position of the minima in the $\bar{R}(\lambda)$ spectrum,
in the second case (curve 2), this correspondence is broken. Curve 3, Fig. 3,
is the $\bar{R}(\lambda)$ of colored glass attesting to the inevitable deformation of the
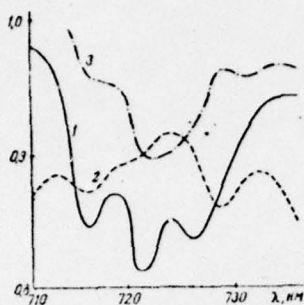
"multipath tray" in the 710-740 nm range.

Fig. 3. Spectra of Diffuse
Reflection: 1-differential:
Nd_2O_3 in optical glass; 2-
differential: Nd_2O_3 in colored
glass; 3-relative: colored
glass powder relative to optical
glass powder.

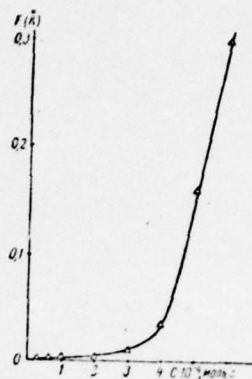Fig. 4. $F(\overline{R})$ as a Function of
Concentration of $Nd(NO_3)_3$ on Al_2O
Surface.

On the Kortüm Method. The Rozenberg method of determining the physi-
cal parameters of the substance of a light-scattering medium, based on the
use of the transfer equation /6/, must be considered the best founded from
the point of view of the theory of light propagation in an optically in-
homogeneous medium. However, the Kortüm method is attracting the attention
of experimenters by virtue of its simplicity. The method is based on the
use of the Gurevich-Kubelka-Munk function:

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha}{\sigma}$$ (2)

(R is the absolute coefficient of diffuse reflection, α and σ are the ab-
sorption and scattering constants respectively) for quantitative photometric
analysis analogous to the Bouguer-Lambert-Behr law /7/. Kortüm believes it
possible in formula (2) to replace the absorption constant α by $2.3\varepsilon C$, where
ε is the molar coefficient of extinction and C is the molar concentration.
Assuming that $2.3\varepsilon C = kn$, (2) can be written in the form

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{2.3\varepsilon C}{\sigma} = \frac{kn}{\sigma}.$$ (3)

The correctness of the Kortüm method raises doubt because in formula (2),
which was obtained through the use of "two-flux" approximation, the replace-
ment of α by $2.3\varepsilon C$ is incorrect. Nonetheless, Kortüm and associates repeatedly
refer to the linear dependence of $F(R)$ on C given constants ε and σ for small
concentrations of adsorbed molecules. This was confirmed in their works by
experimental check. Deviations from linear dependence observed in some cases
where there are small concentrations of adsorbed substance they ascribe to

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side effects, especially those caused by associative or dissociative processes in the surface.

Proceeding from the concept of a light-scattering layer in the form of a "multipath tray," we assume that $F(R)$ as a function of C can in principle not be linear in cases of small concentrations of adsorbed substance (see formulas (1) and (3)).

For an experimental check of the character of the dependence of $F(R)$ on C we used nitrates of rare earth elements as adsorbents. Absorption bands in the spectra of rare earth ions are caused by transitions between 4f levels of electrons screened by the outer shells. As a result the case of the weak field is realized in such a degree that the spectra of ions in the crystals are close to the spectra of free ions /8/. Thanks to this, it is possible to disregard change in ε due to dissociative or associative processes. Fig. 4 presents $F(\bar{R})$ as a function of the concentration of $Nd(NO_3)_3$ to Al_2O_3 derived as the result of measurements of $\bar{R}$ in the maximum of the absorption band when $\lambda = 579$ nm. In this region of the spectrum Al_2O_3 can be viewed as a nonabsorbing standard that, according to Kortüm, permits the use of $\bar{R}$ instead of R in formula (3). The concentration of $2 \cdot 10^{-4}$ mole/g corresponds to this surface coating, when an average of 160 $Å^2$ is required for one molecule of $Nd(NO_3)_3$. Thus, as may be seen in Fig. 4, the linear dependence of $F(\bar{R})$ on C is not observed, when the amount of adsorbed molecules is still insufficient for a monomolecular coating of the entire surface of the adsorbent. The transition from $F(\bar{R})$ to $F(R)$ by the appropriate scaling does not lead to a linear dependence of $F(R)$ on C, /395 the general view of which, despite expectations /9/, remains similar to that presented in Fig. 4.

In conclusion it must again be emphasized that everything that has been said above refers to the particular case where the degree of adsorbent surface covering by molecules is so small that it is possible to ignore light scattering by the adsorbed substance. In those cases where the adsorbed phase itself creates a supplemental optical inhomogeneity in the light-scattering layer as, for example, in the case of capillary condensation, it is impossible to ignore light scattering by the adsorbed phase just as it is impossible to use the model of the "multipath tray" described above. In such cases the problem of obtaining information on the absorption spectra of adsorbed substance from the spectra of diffuse reflection is greatly complicated.

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